Supporting information for

Safe and convenient synthesis of primary N-nitramines in the freon media

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1. General information

The reactions were carried out in 22 cm³ steel autoclave equipment with sapphire windows, magnetic stirrer and pressure and temperature sensors. An auxiliary 13 cm³ steel dosing vessel with sapphire windows and magnetic stirrer was used for preparation of nitrating agents’ solutions. Melting points were obtained on Stuart®, SMP40. ¹H, ¹³C and ¹⁴N NMR spectra were recorded on a Bruker®, AM-300 (300.13, 75.47 and 21.69 MHz, respectively).

X-ray diffraction data for 8c were collected on a Bruker APEX DUO diffractometer (λ(MoKα) = 0.71073 Å, 0-scans with 0.55° step and 10 s per frame exposure, 2θ < 60°). Colorless crystals of C₆H₁₂N₄O₄ at 120 K are monoclinic, space group P2₁/n, a = 6.5740(12), b = 8.3930(15), c = 16.114(3) Å, β = 96.629(4), V = 883.2(3) Å³, Z = 4, d_<sub>calc</sub> = 1.536 g cm⁻³. Intensities of 2570 independent reflections (R_<sub>int</sub> = 0.0216) out of 11189 collected were used in structure solution and refinement. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F² in the anisotropic approximation. Hydrogen atoms connected to nitrogen atoms were found from difference Fourier synthesis and refined in isotropic approximation. All other hydrogen atoms were placed in calculated positions and refined in riding model with U_<sub>iso</sub>(H) = 1.2 U_<sub>eq</sub>(C) of the connected carbon atoms. The refinement converged to R₁ = 0.0360 (calculated for 2235 observed reflections with I>2σ(I)), wR₂ = 0.0930 and GOF = 1.040. All calculations were performed with SHELX software package.¹

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC), reference number 1485396. These data can be obtained free of charge via [http://www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Fluid CF₃CH₂F were obtained from «Linde Gas Rus».

Starting compounds 1,² 2, 6,³,⁴ and 9⁵ were prepared according to reported methods.

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2. Experimental procedures

Synthesis of nitro compounds 3, 4 and 7 (General procedure)

A steel autoclave-reactor containing 5 mmol of substrate 1 or 6 (or 10 mmol of 2) was filled with liquid TFE at room temperature by one third of volume and cooled to 5 °C. DNP (1.19 g, 11 mmol) was placed into an auxiliary dosing vessel which was then closed and filled with the same fluid by half. The obtained DNP solution was slowly added to the reactor (temperature increment by more than 5 °C is to be avoided during reagent addition!). The dosing vessel was twice washed with the fluid (one third of volume) to transfer residual DNP into the reactor. The reaction mixture was stirred at 6 bar and ambient temperature for the time given in Table 1. Then water (2 ml) was added to the reactor to decompose the excess of the nitrating agent. The fluid was removed by decompression. The autoclave was opened and ice water (20 ml) was added to the residue. The resulting mixture was neutralized with sodium hydrocarbonate aqueous solution and extracted with EtOAc (3 × 20 ml). The combined organic extracts were dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure (50 Torr) to afford nitro compound 3, 4, or 7. The yields are given in Table 1.

N,N’-Dimethyl-N,N’-dinitrooxalamide (3a). Colorless solid, 1.03 g (95%). Mp. 123-124 °C (EtOAc) (lit.,⁶ 124 °C).

IR νmax/cm⁻¹ 1732 and 1706 (C=O), 1572 (NO₂), 1345 (NO₂).

¹H NMR (300.13 MHz, DMSO-d₆) δ: 3.65 (s, 6H, CH₃).

¹³C NMR (75.47 MHz, DMSO-d₆) δ: 158.6, 32.5.

N,N’-Dinitro-N,N’-di(n-propyl)oxalamide (3b). Colorless solid, 1.22 g (93%). Mp. 41-42 °C (EtOAc) (lit.,⁷ 44 °C).

IR νmax/cm⁻¹ 1729 and 1706 (C=O), 1576 (NO₂), 1297 (NO₂).

¹H NMR (300.13 MHz, CDCl₃) δ: 4.23-4.02 (m, 4H, NHCH₂), 1.77 (sex, J = 7.4 Hz, 4H, CH₂CH₂CH₃), 1.00 (t, J = 7.4 Hz, 6H, CH₃).

¹³C NMR (75.47 MHz, CDCl₃) δ: 159.0, 47.5, 19.8, 10.8.

¹⁴N NMR (21.69 MHz, CDCl₃) δ: -44.8 (NO₂).

N,N’-Dinitro-N,N’-di(n-pentyl)oxalamide (3c). Light-yellow liquid, 1.48 g (93%). Bp. 124-126 °C (0.65 Torr).

⁶ Kuchurov, I. V.; Fomenkov, I. V.; Zlotin, S. G.; Tartakovsky, V. A. Mendeleev Commun. 2013, 23, 81.
IR \( \nu_{\text{max}} / \text{cm}^{-1} \) 1707 (C=O), 1577 (NO\(_2\)), 1303 and 1254 (NO\(_2\)).

\(^1\)H NMR (300.13 MHz, CDCl\(_3\)) \( \delta \): 3.15 (d t, \( J = 7.7 \text{ Hz} \), \( J = 7.4 \text{ Hz} \), 4H, NHCH\(_2\)), 1.73 (quin, \( J = 7.1 \text{ Hz} \), 4H, NHCH\(_2\)CH\(_2\)), 1.44-1.24 (m, 8H, CH\(_2\)CH\(_2\)CH\(_3\)), 0.91 (t, \( J = 6.6 \text{ Hz} \), 6H, CH\(_3\)).

\(^{13}\)C NMR (75.47 MHz, CDCl\(_3\)) \( \delta \): 158.9, 46.13, 28.5, 25.9, 22.2, 13.9.

\(^{14}\)N NMR (21.69 MHz, CDCl\(_3\)) \( \delta \): -44.7 (NO\(_2\)).

Anal. Calcd for C\(_{12}\)H\(_{22}\)N\(_4\)O\(_6\): C, 45.3; H, 7.0; N, 17.6%. Found: C, 45.1; H, 7.3; N, 17.3.

**N,N’-Dicyclohexyl-N,N’-dinitrooxalamide (3d).** Colorless solid, 1.08 g (63%). Mp. 128 °C (EtOAc) (lit., \(^8\) 130 °C).

IR \( \nu_{\text{max}} / \text{cm}^{-1} \) 1728 and 1703 (C=O), 1563 (NO\(_2\)), 1297 (NO\(_2\)).

\(^1\)H NMR (300.13 MHz, CDCl\(_3\)) \( \delta \): 4.66 (t t, \( J = 12.2 \text{ Hz} \), \( J = 3.6 \text{ Hz} \), 2H, C\(_3\)H), 2.25-1.16 (m, 20H, C\(_2\)H\(_2\)C\(_2\)H\(_2\)C\(_2\)H\(_2\)C\(_2\)H\(_2\)).

\(^{13}\)C NMR (75.47 MHz, CDCl\(_3\)) \( \delta \): 159.3, 59.7, 27.9, 26.1, 24.9.

\(^{14}\)N NMR (21.69 MHz, CDCl\(_3\)) \( \delta \): -39.1 (NO\(_2\)).

Anal. Calcd for C\(_{24}\)H\(_{22}\)N\(_4\)O\(_6\): C, 49.1; H, 6.5; N, 16.4%. Found: C, 49.05; H, 6.6; N, 16.3.

**Ethyl N-ethyl-N-nitrocarbamate (4a).** Light-yellow liquid, 1.54 g (95%).

IR \( \nu_{\text{max}} / \text{cm}^{-1} \) 1772 (C=O), 1576 (NO\(_2\)), 1310 (NO\(_2\)), 1222 (C-O).

\(^1\)H NMR (300.13 MHz, DMSO-d\(_6\)) \( \delta \): 4.32 (q, \( J = 7.1 \text{ Hz} \), 2H, NCH\(_2\)CH\(_3\)), 4.05 (q, \( J = 7.0 \text{ Hz} \), 2H, OCH\(_2\)CH\(_3\)), 1.29 (t, \( J = 7.1 \text{ Hz} \), 3H, NCH\(_2\)CH\(_3\)), 1.21 (t, \( J = 7.0 \text{ Hz} \), 3H, OCH\(_2\)CH\(_3\)).

**Ethyl N-cyclohexyl-N-nitrocarbamate (4b).** Colorless liquid, 2.01 g (93%). Bp. 93-95 °C (0.6 Torr). \( n_D^{20} \) 1.4650.

IR \( \nu_{\text{max}} / \text{cm}^{-1} \) 1769 (C=O), 1580 (NO\(_2\)), 1304 (NO\(_2\)), 1217 (C-O).

\(^1\)H NMR (300.13 MHz, CDCl\(_3\)) \( \delta \): 4.34 (q, \( J = 7.1 \text{ Hz} \), 2H, NCH\(_2\)CH\(_3\)), 1.95-1.06 (m, 10H, CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)), 1.35 (t, \( J = 7.1 \text{ Hz} \), 3H, CH\(_2\)CH\(_3\)).

\(^{13}\)C NMR (75.47 MHz, CDCl\(_3\)) \( \delta \): 151.3, 64.6, 61.2, 29.5, 25.9, 25.1, 14.0.

\(^{14}\)N NMR (21.69 MHz, CDCl\(_3\)) \( \delta \): -40.5 (NO\(_2\)).

Anal. Calcd for C\(_9\)H\(_{16}\)N\(_2\)O\(_4\): C, 50.0; H, 7.5; N, 13.0%. Found: C, 50.3; H, 7.4; N, 12.9.

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Ethyl N-tert-butyl-N-nitrocarbamate (4c). Yellow liquid, 1.82 g (95%). Bp. 49 °C (0.8 Torr) (lit.,9 49-51 °C at 0.4 Torr). nD20 1.4335.

IR νmax/cm⁻¹ 1769 and 1745 (C=O), 1557 (NO2), 1328 (NO2), 1270 (C-O).

1H NMR (300.13 MHz, CDCl3) δ: 4.32 (q, J = 7.1 Hz, 2H, CH2), 1.50 (s, 9H, CH3), 1.33 (t, J = 7.2 Hz, 3H, CH2CH3).

13C NMR (75.47 MHz, CDCl3) δ: 151.6, 64.7, 62.2, 27.2, 13.9.

14N NMR (21.69 MHz, CDCl3) δ: -37.3 (NO2).

Diethyl ethane-1,2-diylbis(nitrocarbamate) (7a). Colorless solid, 1.44 g (98%). Mp. 81-82 °C (EtOAc) (lit.,6 80-82 °C).

IR νmax/cm⁻¹ 1735 (C=O), 1586 (NO2), 1280 (NO2) 1241 (C-O).

1H NMR (300.13 MHz, DMSO-d6) δ: 4.39 (s, 4H, C2NNO2), 4.25 (q, J = 7.1 Hz, 4H, OCH2CH3), 1.24 (t, J = 7.1 Hz, 6H, OCH2CH3).

Diethyl propane-1,3-diylbis(nitrocarbamate) (7b). Yellow liquid, 1.40 g (91%). Bp. 131-135 °C (0.7 Torr). nD20 1.4789.

IR νmax/cm⁻¹ 1773 and 1741 (C=O), 1577 (NO2), 1314 (NO2), 1235 (C-O).

1H NMR (300.13 MHz, CDCl3) δ: 4.36 (q, J = 7.1 Hz, 4H, CH2Me), 4.13 (t, J = 7.1 Hz, 4H, NHCH2), 2.10 (quin, J = 7.1 Hz, 2H, CH2CH2CH2), 1.36 (t, J = 7.2 Hz, 6H, CH2CH3).

13C NMR (75.47 MHz, CDCl3) δ: 150.4, 65.0, 46.6, 25.6, 14.1.

14N NMR (21.69 MHz, CDCl3) δ: -43.9 (NO2).

Anal. Calcd for C9H16N4O8: C, 35.1; H, 5.2; N, 18.2%. Found: C, 35.4; H, 5.45; N, 18.2.

Diethyl cyclohexane-1,2-diylbis(nitrocarbamate) (7c). Yellow liquid, 1.56 (90%). Bp. 94-95 °C (0.65 Torr). nD20 1.4837.

IR νmax/cm⁻¹ 1769 (C=O), 1586 (NO2), 1335 and 1310 (NO2), 1234 and 1200 (C-O).

1H NMR (300.13 MHz, CDCl3) δ: 5.10-4.98 (m, 2H, CH), 4.33 (q, J = 7.1 Hz, 4H, OCH2), 2.16-1.78 (m, 8H, CHCH2CH2), 1.34 (t, J = 7.2 Hz, 6H, CH3).

13C NMR (75.47 MHz, CDCl3) δ: 150.9, 65.0, 46.6, 25.6, 14.1.

14N NMR (21.69 MHz, CDCl3) δ: -42.8 (NO2).

Anal. Calcd for C12H20N4O8: C, 41.4; H, 5.8; N, 16.1%. Found: C, 41.3; H, 5.8; N, 16.25.

One-pot synthesis of N-nitramines 5, 8 and 11 (General procedure)

A steel autoclave-reactor containing 5 mmol of substrate 1 or 6 (10 mmol of 2 or 9) was filled with liquid TFE at ambient temperature by one third of volume and cooled to 5 °C. DNP (1.19 g, 11 mmol) was placed into an auxiliary dosing vessel which was then closed and filled with the same fluid by half. The obtained DNP solution was slowly added to the reactor (temperature increment by more than 5 °C is to be avoided during reagent addition!). The dosing vessel was twice washed with the fluid (one third of volume) to transfer residual DNP into the reactor. The reaction mixture was stirred at 6 bar and ambient temperature for the time given in Table 1. Once the nitration completed, the autoclave was cooled to 5 °C and liquid ammonia (1.3 ml, 50 mmol) was gradually added with intensive stirring by the syringe pump at flow-rate 0.1÷0.2 ml/min (temperature increment by more than 10 °C is to be avoided during reagent addition!). The reaction mass was stirred at ambient temperature for 20 min. Then the fluid and the excess of ammonia were removed via decompression and the autoclave was opened.

Isolation of nitramines 5a-d (General procedure)

After decompression, 96% EtOH (40 ml) was added to the residue and the mixture was stirred at 50 °C for 10 min. The solvent was evaporated under reduced pressure (30 Torr). Diethyl ether (40 ml) was added to the residue and the resulting suspension was vigorously stirred for 5-10 min. The solid (oxamide and ammonium nitrate) was filtered off and washed with diethyl ether (2 x 15 ml). The combined ether solution was evaporated to afford corresponding nitramine 5a-d. The yields are given in Table 1.

N-methylnitramine (5a). Colorless solid, 0.61 g (80%). Mp. 36 °C (Et₂O), Bp. 82 °C (12 Torr) (lit., 10 80-85 °C at 10 Torr).

IR ν max/cm⁻¹ 3432 and 3387 (NH), 1572 (NO₂), 1342 (NO₂).

¹H NMR (300.13 MHz, CDCl₃) δ: 9.01 (br s, H, NH), 3.18 (s, 3H, CH₃).

¹³C NMR (75.47 MHz, CDCl₃) δ: 32.6.

¹⁴N NMR (21.69 MHz, CDCl₃) δ: -25.6 (NO₂).

Anal. Calcd for CH₄N₂O₂: C, 15.8; H, 5.3; N, 36.8%. Found: C, 15.8; H, 5.2; N, 36.7.

N-(n-propyl)nitramine (5b). Colorless liquid, 0.95 g (91%). Bp. 62-62 °C (0.8 Torr) (lit., 11 47-48 °C at 0.3 Torr). nD 20 1.4582.

IR ν max/cm⁻¹ 3299br (NH), 1572 (NO₂), 1322 (NO₂).

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$^1$H NMR (300.13 MHz, CDCl$_3$) δ: 8.61 (br s, H, NH), 3.61-3.48 (m, 2H, NHCH$_2$), 1.65 (sex, $J = 7.3$ Hz, 2H, CH$_2$CH$_2$CH$_3$), 0.98 (t, $J = 7.4$ Hz, 3H, CH$_3$).

**N-\textit{(n-pentyl)}nitramine (5c).** Colorless liquid, 1.14 g (86%). Bp. 86 °C (0.8 Torr) (lit.,$^{12}$ 60-62 °C at 0.02 Torr). $n_D^{20}$ 1.4595.

IR $\nu_{\text{max}}$/cm$^{-1}$ 3287 and 3139 (NH), 1577 (NO$_2$), 1331 (NO$_2$).

$^1$H NMR (300.13 MHz, CDCl$_3$) δ: 8.80 (br s, H, NH), 3.62-3.48 (m, 4H, NHCH$_2$), 1.60 (quin, $J = 6.8$ Hz, 4H, NHCH$_2$CH$_2$), 1.39-1.27 (m, 8H, CH$_2$CH$_2$CH$_3$), 0.89 (t, $J = 6.2$ Hz, 6H, CH$_3$).

$^{13}$C NMR (75.47 MHz, CDCl$_3$) δ: 46.4, 28.8, 26.5, 22.2, 13.9.

$^{14}$N NMR (21.69 MHz, CDCl$_3$) δ: -22.6 (NO$_2$).

Anal. Calcd for C$_5$H$_{12}$N$_2$O$_2$: C, 45.4; H, 9.15; N, 21.2%. Found: C, 45.7; H, 9.0, N, 21.25.

**N-cyclohexynitramine (5d) (from 1d).** Yellow viscous liquid, 0.60 g (53%). Bp. 98 °C (0.7 Torr) (lit.,$^{13}$ 121-122 °C at 3 Torr). $n_D^{20}$ 1.5000.

IR $\nu_{\text{max}}$/cm$^{-1}$ 3278 and 3137 (NH), 1576 (NO$_2$), 1339 (NO$_2$).

$^1$H NMR (300.13 MHz, CDCl$_3$) δ: 8.75 (br s, H, NH), 4.02-3.88 (m, H, CH), 2.07-1.15 (m, 10H, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$).

$^{13}$C NMR (75.47 MHz, CDCl$_3$) δ: 55.5, 30.3, 25.3, 24.3.

$^{14}$N NMR (21.69 MHz, CDCl$_3$) δ: -28.8 (NO$_2$).

Anal. Calcd for C$_6$H$_{12}$N$_2$O$_2$: C, 50.0; H, 8.4; N, 19.4%. Found: C, 50.0; H, 8.4, N, 19.5.

**Isolation of nitramines 5d-f (General procedure)**

After decompression, the residue was extracted with diethyl ether (4 × 15 ml). The combined organic extracts were evaporated to afford ethylcarbamate (quantitative). Ethanol (96%, 40 ml) was added to solid residue (a mixture of ammonium nitrate and N-alkynitramine 5 ammonium salt) and the mixture was stirred at 55 °C for 10 min. The solvent was removed under reduced pressure (30 Torr). Diethyl ether (40 ml) was added to the residue and the resulting suspension was vigorously stirred for 5-10 min. The solid (ammonium nitrate) was filtered off, and washed with diethyl ether (2 × 15 ml). The combined ether solution was evaporated to afford corresponding nitramines 5d-f. The yields are given in Table 1.

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**N-cyclohexyl nitramine (5d).** Yellow viscous liquid, 0.87 g (76%). Characteristics of the product were similar to those for compound 5d obtained from 1d.

**N-ethyl nitramine (5e).** Colorless liquid, 0.84 g (93%). Bp. 82-83 °C (8 Torr) (lit., 14 98 °C at 15 Torr). \( n_D^{20} \) 1.4545. IR \( v_{\text{max}}/\text{cm}^{-1} \) 3281 br (NH), 1574 (NO\(_2\)), 1322 (NO\(_2\)).

\(^1\)H NMR (300.13 MHz, CDCl\(_3\)) \( \delta \): 9.14 (br. s, NH), 3.59 (d q, \( J = 7.0 \) Hz, \( J = 1.9 \) Hz, 2H, \( CH_2 \)), 1.22 (t, \( J = 7.2 \) Hz, 3H, \( CH_3 \)).

**N-tert-butyl nitramine (5f).** \(^1\)H NMR (300.13 MHz, CDCl\(_3\)) \( \delta \): 8.60 (br s, H, NH), 1.39 (s, 9H, \( CH_3 \)).

**Isolation of nitramines 8a-c and 11 (General procedure)**

After decompression, the residue was extracted with diethyl ether (4 × 15 ml) (for 8a-c) to afford ethyl carbamate by-product (0.85 g, 98%). Cold water (10 ml) was added to the residue and the mixture was acidified by 10 N HCl (2 ml) with vigorous stirring. The precipitate was filtrated, washed with water (2 × 15ml) and dried at ambient temperature (70 Torr) or to afford corresponding nitramines 8a and 8c. Alternatively, the aqueous mixture was extracted with ethyl acetate (4 × 15 ml). The combined organic extracts were dried over anhydrous MgSO\(_4\). The solvent was evaporated under reduced pressure (50 Torr) to afford corresponding nitramines 8b and 11.

**1,2-Ethylenedinitramine (8a).** Colorless solid, 0.70 g (93%). Mp. 177 °C (H\(_2\)O) (lit., 15 180 °C).

IR \( v_{\text{max}}/\text{cm}^{-1} \) 3236 and 3117 (NH), 1594 (NO\(_2\)), 1351 (NO\(_2\)).

\(^1\)H NMR (300.13 MHz, DMSO-d\(_6\)) \( \delta \): 12.08 (br s, H, NH), 3.59 (s, 4H, \( CH_2 \)).

\(^{14}\)N NMR (21.69 MHz, DMSO-d\(_6\)) \( \delta \): -26.0 (NO\(_2\)).

**1,3-Propylenedinitramine 8b.** Colorless solid, 0.71 g (86%). Mp. 66-67 °C (EtOAc) (lit., 16 67 °C).

IR \( v_{\text{max}}/\text{cm}^{-1} \) 3320 and 3099 (NH), 1579 (NO\(_2\)), 1314 (NO\(_2\)).

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$^1$H NMR (300.13 MHz, DMSO-d$_6$) $\delta$: 12.00 (br s, H, NH), 3.45 (t, $J = 7.0$ Hz, 4H, NHCH$_2$), 1.76 (quin, $J = 6.9$ Hz, 2H, CH$_2$CH$_2$CH$_2$).

$^{14}$N NMR (21.69 MHz, DMSO-d$_6$) $\delta$: -25.6 (NO$_2$)

1,2-Cyclohexanediyldinitramine 8c. Colorless solid, 0.89 g (87%). Mp. 150 °C (H$_2$O) (lit.,$^{17}$ 163 °C).

IR $\nu_{\text{max}}$/cm$^{-1}$ 3315 and 3223 (NH), 1587 and 1557 (NO$_2$), 1297 (NO$_2$).

$^1$H NMR (300.13 MHz, DMSO-d$_6$) $\delta$: 12.13 (br s, 2H, NH), 4.02-3.81 (m, 2H, CH), 2.14-1.89 (m, 2H, CHCH$_2$(B)CH$_2$), 1.79-1.55 (m, 2H, CHCH$_2$(A)CH$_2$), 1.4-1.11 (m, 4H, CHCH$_2$CH$_2$).

$^{13}$C NMR (75.47 MHz, DMSO-d$_6$) $\delta$: 55.7, 29.5, 23.5.

$^{14}$N NMR (21.69 MHz, DMSO-d$_6$) $\delta$: -27.3 (NO$_2$).

Anal. Calcd for C$_6$H$_{12}$N$_4$O$_4$: C, 35.3; H, 5.9; N, 27.4%. Found: C, 35.6; H, 6.0; N, 27.4.

(2-Nitramino)ethyl carbamate (11). Colorless solid, 1.10 g (94%). Mp. 84 °C (EtOAc).

IR $\nu_{\text{max}}$/cm$^{-1}$ 3490 (NH$_2$), 3367 and 3306 (NH), 3189 and 3110 (NH$_2$), 1710 (C=O), 1576 (NO$_2$), 1317 (NO$_2$), 1238 (C-O).

$^1$H NMR (300.13 MHz, DMSO-d$_6$) $\delta$: 12.10 (br s, H, NH), 6.54 (br s, 2H, NH$_2$), 4.04 (t, $J = 5.3$ Hz, 2H, OCH$_2$), 3.61 (q, $J = 4.8$ Hz, 2H, NHCH$_2$).

$^{13}$C NMR (75.47 MHz, DMSO-d$_6$) $\delta$: 156.4, 59.6, 44.6.

$^{14}$N NMR (21.69 MHz, DMSO-d$_6$) $\delta$: -25.9 (NO$_2$).

Anal. Calcd for C$_3$H$_7$N$_3$O$_4$: C, 24.2; H, 4.7; N, 28.2%. Found: C, 24.2; H, 4.8; N, 28.05.

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3. NMR data for compounds 3, 4, 5, 7, 8 and 11

$^1$H NMR for $N,N'$-dimethyl-$N,N'$-dinitrooxalamide (3a)

![NMR Spectra](image)

The Bruker Axcend AV400 NMR. Operator: Ivanov D.A.; Date: Dec 2011; Solv: DMSO-d6; Temple: Unique. Signal: 4.18; Scans: 100; SW: 600 Hz; Gv: 750 Hz; FID: 3000 Hz; Sinc: 4.18; 300 K 5 December 2011  Opr. Struchkova M.I.; Solv: DMSO-d6;
$^{13}$C NMR for $N,N'$-dimethyl-$N,N'$-dinitrooxalamide (3a)
$^1$H NMR for $N,N'$-dinitro-$N,N'$-di(n-propyl)oxalamide (3b)
\(^{13}\)C NMR for \(N,N'\)-dinitro-\(N,N'\)-di(\(n\)-propyl)oxalamide (3b)

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500 SF=75.47 MHz \([^{13}\)C\] SF=225K SW=161.14 O1=3001 PW=0.30 AQ=0.101 IDE=1.00 NS=156 SK=6.52 TE=298K 11 November 2015 Oper: Darva E.D.; Solv: CDCl3;
$^{14}$N NMR for $N,N'$-dinitro-$N,N'$-di($n$-propyl)oxalamide (3b)

Chemical structure of 3b is shown with two nitro groups and a di($n$-propyl)oxalamide group.

Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=21.69 MHz $^{14}$N; SF=8K SW=65785 O1=9510 PW=10.0 AQ=0.050 RD=0.05 NS=355 SIR=7317.05 TE=298K 11 November 2015 Op: Daeva E.D.; Solv: CDCl3

[Chemical structure image]
$^1$H NMR for $N,N'$-dinitro-$N,N'$-di(\textit{n}-pentyl)oxalamide (3c)
$^{13}$C NMR for $N,N'$-dinitro-$N,N'$-di($n$-pentyl)oxalamide (3c)

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500 SF=75.47 MHz; [13C] SF=32K SW=181.14 OI=8301 PW=10.0 AQ=0.901 RD=1.00 NS=256 SK=6.44 TE=297K 16 November 2015 Oper: Darva E.D.; Solv: CDCl3;
$^{14}$N NMR for $N,N'$-dinitro-$N,N'$-di(n-pentyl)oxalamide (3c)

© Zolinsk Institute of Organic Chemistry, Moscow; Bruker AM500 SF=21.69 MHz $^{14}$N SI=8K SW=5785 Q1=9510 PW=10.0 AQ=0.050 KD=0.05 NS=16 SK=n1705 TE=297K 16 November 2013 Opr: Dava E.D.; Solv: CDCl3

$\text{NO}_2$ $\text{N}$ $\text{O}$ $\text{N}$ $\text{NO}_2$

3c

1400 1200 1000 800 600 400 200 0 -200 -400 -600 -800 -1000 -1200 ppm
$^1$H NMR for $N,N'$-dicyclohexyl-$N,N'$-dinitrooxalamide (3d)
$^{13}$C NMR for $N,N'$-dicyclohexyl-$N,N'$-dinitrooxalamide (3d)
$^{14}$N NMR for $N,N'$-dicyclohexyl-$N,N'$-dinitrooxalamide (3d)

Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500 SF=21.69 MHz; $^{14}$N SF=8K SW=21758 CI=8000 PW=10.0 AQ=0.091 RD=0.30 NS=182 SR=7213.73 TE=290K. 16 January 2016. Oper: Struchkova M.I.; Solv: CDC13.
$^1$H NMR for ethyl $N$-ethyl-$N$-nitrocarbamate (4a)

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500 SI=300.13 MHz (1H) S=16K SW=6002 O1=2500 PW=90 AQe=1.352 KD=3.00 NS=1 SSk=10.55 TE=299K 24 July 2015 Opr: Struchkova M.I.; Solv: DMSO-d6;
1H NMR for Ethyl N-cyclohexyl-N-nitrocarbamate (4b)
$^{13}$C NMR for ethyl $N$-cyclohexyl-$N$-nitrocarbamate (4b)

Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500 SF=75.47 MHz ($^{13}$C) $S=22$K $SW=18114$ $O1=8301$ $PW=10.0$ $AQ=0.901$ $RD=1.06$ NS=290 Sk=4.51 $T_{1}=290 K$ 21 January 2016 Opr: Davva E.D.; Solv: CDCl$_3$.
\[ ^{14} \text{N NMR for ethyl} \text{ N-cyclohexyl-N-nitrocarbamate (4b)} \]
$^1$H NMR for ethyl $N$-tert-butyl-$N$-nitrocarbamate (4c)
$^{13}$C NMR for ethyl $N$-tert-butyl-$N$-nitrocarbamate (4c)
$^{14}$N NMR for ethyl $N$-tert-butyl-$N$-nitrocarbamate (4c)
$^{1}H$ NMR for diethyl ethane-1,2-diylbis(nitrocarbamate) (7a)
$^{13}$C NMR for diethyl ethane-1,2-diylbis(nitrocarbamate) (7a)
$^1$H NMR for diethyl propane-1,3-diylbis(nitrocarbamate) (7b)
$^{13}$C NMR for diethyl propane-1,3-diylbis(nitrocarbamate) (7b)

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500 SF=75.47 MHz [$^{13}$C] S=32K SW=18114 O1=801 PW=10.0 AQ=0.0 R=1.06 NS=150 SK=4.03 T1=298K 2 December 2015 Opr: Dava E.D.; Solv: CDCl3

Chemical shifts (ppm): 15.43, 43.26, 53.60, 65.43, 71.63, 77.10, 78.69, 85.95, 14.095
$^{14}\text{N}$ NMR for diethyl propane-1,3-diylbis(nitrocarbamate) (7b)
$^1$H NMR for diethyl cyclohexane-1,2-diylbis(nitrocarbamate) (7c)
$^{13}$C NMR for diethyl cyclohexane-1,2-diylbis(nitrocarbamate) (7c)

Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500 8F=75.47 MHz $^{[13C]}$ $S=32$K $W=181$Hz $O=801$ PW=1.06 $A=354$ $R=5.94$ $T=298$K 9 December 2015 Opr: Daves E.D.; Solv: CDCl3.
$^{14}$N NMR for diethyl cyclohexane-1,2-diylbis(nitrocarbamate) (7c)

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500 SF=21.69 MHz $^{14}$N SF=8K SW=85785 O1=9510 PW=0.0 AQ=0.00 RD=0.05 NS=11378 SK=701775 TE=298K 9 December 2015  Opr: Dateva E.D.; Solv: CDCl3;
$^1$H NMR for $N$-methylnitramine ($5a$)
$^{13}$C NMR for N-methylnitramine (5a)

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500 SF=75.47 MHz $^{13}$C S=32K SW=18114.81=801 PW=100.0 AQ=0.901 RD=1.06 NS=1206 SK=8.22 TE=298K 5 August 2015 Opr: Daseva E.D.; Solv: CDCl3;
$^{14}N$ NMR for $N$-methylnitramine (5a)
$^1$H NMR for $N$-(n-propyl)nitramine (5b)
\(^1\)H NMR for \(N\)-(n-pentyl)nitramine (5c)

Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500 SF=300.13 MHz (1H) S1=16K SW=6010 O1=2401 PW=80 AQ=1.352 K0=1.00 NS=1 SSk=8.40 Tl=298K 9 November 2015 Opr: Daraeva E.D.; Solv: CDCl3
$^1$H NMR for $N$-cyclohexylnitramine (5d)
$^{13}$C NMR for $N$-cyclohexyl nitramine (5d)

Chemical shifts: 77.5, 71.5, 76.9, 5.2, 5.4, 30.5, 25.1, 24.3 ppm.
$^{14}$N NMR for $N$-cyclohexyl nitramine (5d)
$^1$H NMR for $N$-ethylnitramine (5e)

Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500, SF=300.13 MHz (1H) S=16K SW=8010 O1=2401 PW=50 AQ=1.352 JD=1.00 NS=1 SSK=9.30 TF=290K 2 June 2016 Oper: Danva E.D.; Solv: CDCl$_3$
$^{1}$H NMR for 1,2-ethylenedinitramine (8a)

Zolimsky Institute of Organic Chemistry, Moscow; Bruker AM360 500.13 MHz (1H) $\delta=18K$ $\Delta$W=6001 $\tilde{O}t=2401$ $\tilde{P}W=90$ $\tilde{A}P=1.352 \ K1=1.06$ $\tilde{N}S=1$ $SK=0.09$ $\tilde{T}t=298K$ 25 November 2015 Op: Daraia E.D.; Solv: DMSO-d6;
$^{14}$N NMR for 1,2-ethylenedinitramine (8a)

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300, SF=21.69 MHz, $^{14}$N, SI=8K, SW=5678.81, PW=0.0, AQ=0.030, RD=0.05, NS=1245, Sk=7, T=17.03, TE=298K. 16 December 2015. Oper: Davvy E.D.; Solv: DMSO-d6.
$^1$H NMR for 1,3-propylenedinitramine (8b)

Zelinsky Institute of Organic Chemistry, Moscow; Bruker AMX600 SF=300.13 MHz (1H) S=16K SW=6000 OI=2401 PW=90 AQP=1.352 KD=1.00 NS=1 SK=0.97 TI=298K 14 December 2015 Opr: Danva E.D.; Solv: DMSO–d6;
$^{14}$N NMR for 1,3-propylenedinitramine (8b)

Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500 SF=216 MHz; $^{14}$N SF=88K SW=858500 T1=9310 PW=60.3 AQ=0.30 KID=0.45 NS=1501 Sck=71705 TE=298K 16 December 2015 Oper: Davesa E.D.; Solv: DMSO-d6.
$^1$H NMR for 1,2-cyclohexanediylidinitramine (8c)
$^{13}$C NMR for 1,2-cyclohexanediyldinitramine (8c)

[Chemical Structure Image]
$^{14}$N NMR for 1,2-cyclohexanediyldinitramine (8c)

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM500 SF=21.69 MHz $^{14}$N; SE=8K SW=5878 O1=9310 PW=10.0 AQ=0.030 RD=0.05 NS=5427 SK=7X1705 TE=298K 10 December 2015  Opr: Darva E.D.; Solv: DMSO-d6;
$^{1}$H NMR for (2-nitramino)ethyl carbamate (11)

O 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

1.5 1.3 1.0 0.8 0.6

O 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

1.2 0.8 0.6

O

NH$_2$

H$_2$N

O

NO$_2$

O

N

H
$^{13}$C NMR for (2-nitramino)ethyl carbamate (11)
$^{14}$N NMR for (2-nitramino)ethyl carbamate (11)
4. General view of molecule 8c in crystal